

The Surface Tension of Water and of Certain
Dilute Aqueous Solutions, Determined
by the Method of Ripples.

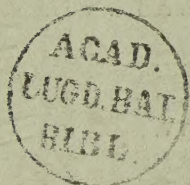
A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

N. ERNEST DORSEY.

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THE SURFACE TENSION OF WATER AND OF CERTAIN DILUTE AQUEOUS SOLUTIONS, DETERMINED BY THE METHOD OF RIPPLES. I.

BY N. ERNEST DORSEY.

INTRODUCTION.

PREVIOUS observers have found that the surface tension of most aqueous solutions is a linear function of the concentration ; but they have worked on no solution more dilute than about one-half normal (a normal solution is one that contains in one liter of the solution as many grams of the salt as there are units in the molecular weight of the salt, the molecular weight of hydrogen being taken as two). It seems, therefore, desirable to determine, if possible, the surface tension of more dilute solutions ; and this work was undertaken at the suggestion of Professor J. S. Ames in the spring of 1895, for the purpose of studying solutions as dilute as possible. Most of the time since then has been spent in studying the various methods, and in perfecting the method of ripples, which appeared to offer fewer theoretical objections than any other.

The arrangement of apparatus finally adopted gives an average departure from the mean of several observations of not more than one-seventh of one per cent. Though different samples of water may give results that differ among themselves by more than this amount, still in the entire series of twenty-one samples of water the average departure of a single observation from the mean was but one-fifth of one per cent. This compares very favorably with the results obtained by any other method.

This spring determinations of the surface tensions of a few solutions were made at concentrations varying from one-tenth normal to normal, and the values found lie upon straight lines starting from the value for pure water.

HISTORICAL AND CRITICAL.

Among those who have worked on the surface tension of aqueous salt solutions may be mentioned Frankenheim,¹ Buliginsky,² Valson,³ Quincke,⁴ Lippmann,⁵ P. Volkmann,⁶ O. Rother,⁷ Traube,⁸ Röntgen and Schneider,⁹ Klupathy,¹⁰ Goldstein,¹¹ Jäger,¹² N. Kasanskine,¹³ Canestrini,¹⁴ Sentis.¹⁵

Excepting Sentis, Jäger, and Klupathy, they all used the method of capillary tubes, and Quincke supplemented this with his method of large bubbles. All determinations of the surface tension from the measured rise of the liquid in capillary tubes involve an assumption in regard to the contact angle, *i. e.*, in regard to the angle included between the wall of the tube and the tangent to the liquid surface at the *point of contact with the tube*. This angle cannot be measured, for by any possible method we must measure the inclination of a finite arc, and as the surface extends on one side only of the point at which we desire the inclination, the finite arc whose inclination we measure must lie entirely on one side of the point of contact. Hence every measured value of this angle will necessarily be too large. This is probably the reason Professor Quincke obtains finite contact angles for liquids that wet the glass in contact with them.

Another objection to measuring the surface tensions of solutions at the line of intersection of three bodies, solution, air and glass, is that probably the tensions of both the solution-air and the solution-glass surfaces change with the concentration of the solution, so that the results obtained involve two changes which can not be separated. This renders the interpretation of the results very diffi-

¹ Pogg. Ann., 37, 409, 1836.

⁶ Wied. Ann., 17, 353, 1882.

² Pogg. Ann., 134, 440, 1868; A. ch. ph. (4), 20, 361, 1870.

³ C. rend., 74, 103, 1872.

⁷ Wied. Ann., 21, 576, 1884.

⁴ Pogg. Ann., 160, 337 and 560, 1877.

⁸ Jour. f. pr. ch., 31, 192, 1885.

⁵ Wied. Ann., 11, 316, 1880.

⁹ Wied. Ann., 29, 165, 1886.

¹⁰ Math. u. naturwiss. Ber. aus Ungarn, 5, 101, 1887; Wied. Ann. Beibl., 12, 750, 1888.

¹¹ Zeitschr. f. phys. chem., 5, 233, 1890.

¹² Acad. d. Wiss. in Wein, 100^{2A}, 493, 1891.

¹³ J. de la Soc. phys. chem. russe, 23, 468, 1891; Jour. de Phys. (3), 1, 406, 1892.

¹⁴ Riv. Sc. ind., p. 33, 1892; Wied. Ann. Beibl., 16, 335, 1892.

¹⁵ Journ. de Phys. (2), 6, 571, 1887; Thesis published at Paris, February, 1897 Jour. de Phys. (3), 6, 183, 1897.

cult. Jäger used a method depending on the relation between the diameter of a capillary tube and the distance it must be immersed in the liquid in order that the same air pressure might cause steady streams of bubbles of the same size to issue from it and from another tube of known diameter immersed to a fixed depth. He determined this relation empirically from experiments on water, and he accepted the results of Brunner and of Wolf as correct. Quincke's work on flat bubbles has been discussed in several papers and seems to be not very satisfactory. From this we see that, excepting the work done by Sentis and by Klupathy, the determinations of the surface-tensions of solutions are not all that can be desired.

Sentis employed an entirely different method, and one that appears to be very free from objections. He draws the liquid up into a capillary tube, then removes the tube from the liquid and allows the liquid to run out so as to form a drop around the end of the tube. This drop supports a certain length liquid column in the tube. He then measures the maximum diameter of the drop, focuses a microscope on the meniscus in the tube, and slowly raises below the tube a beaker of the liquid. When the liquid in the beaker reaches the drop, the column in the tube falls; the position of the beaker is now noted and it is then again slowly raised until the meniscus in the tube has come back to its previous position, and the position of the beaker is then noted. The vertical distance between these two positions of the beaker is (after certain corrections are made) the height the liquid will rise in a tube for which the contact angle is zero and whose radius is equal to that of the drop. His individual determinations may differ by one-half of a per cent., but generally they agree very well.

In the present work it was desired to use a method entirely independent of the mutual action between the liquid and a solid; and the only methods so far devised that completely satisfy this condition are Lenard's¹ method of vibrating falling drops, the method of Eötvös,² that employed by Sentis, and the method of ripples, which was first successfully used by Lord Rayleigh.³ Sentis' method, as

¹ Wied. Ann., 30, 209, 1887.

² Wied. Ann., 27, 448, 1886.

³ Phil. Mag. (5), 30, 386, 1890; Theory of Sound, Vol. II., p. 344.

described in his first paper¹ did not seem very satisfactory; and, of the others mentioned, Lord Rayleigh's appeared to be the most promising, and is the one finally adopted.

METHOD OF RIPPLES.

This method is based on the relation between the surface tension of a liquid and the velocity of propagation, on its surface, of a train of small waves of given period. This was deduced by Lord Kelvin² for the case of infinitely small waves on the surface of a perfect liquid of given depth. His formula is

$$V^2 = \left(\frac{g\lambda}{2\pi} + \frac{2\pi T}{\rho\lambda} \right) \tanh \frac{2\pi h}{\lambda}.$$

Here V is the velocity of propagation; λ is the wave-length; T is the surface tension; ρ is the density; h is the depth of the liquid; and g is the acceleration of gravity. If n is the frequency of the waves we can write this equation thus:—

$$T = \rho \left(\frac{\lambda^3 n^2}{2\pi} \coth \frac{2\pi h}{\lambda} - \frac{g\lambda^2}{4\pi^2} \right).$$

Now
$$\coth \frac{2\pi h}{\lambda} = \frac{1 + \varepsilon^{-\frac{4\pi h}{\lambda}}}{1 - \varepsilon^{-\frac{4\pi h}{\lambda}}} = 1 + 2\varepsilon^{-\frac{4\pi h}{\lambda}}$$

approximately if h is large.

In this work h is never less than 1.1 cm., and λ is never as great as 0.5 cm. Hence

$$\frac{4\pi h}{\lambda} \not\approx 25 \quad \therefore \coth \frac{2\pi h}{\lambda} \not\approx 1 + 2\varepsilon^{-25}.$$

This shows that we may consider $\coth \frac{2\pi h}{\lambda} = 1$, and may write the equation

$$T = \rho \left(\frac{\lambda^3 n^2}{2\pi} - \frac{g\lambda^2}{4\pi^2} \right).$$

¹ Journ. de Phys. (2), 6, 571, 1887.

² Phil. Mag. (4), 42, 375, 1871.

Lamb¹ gives the more exact formula for the case of a liquid of infinite depth

$$V = \left(\frac{\rho - \rho'}{\rho + \rho'} \frac{g\lambda}{2\pi} + \frac{2\pi T}{(\rho + \rho')\lambda} \right)$$

or

$$T = (\rho + \rho') \left(\frac{\lambda^3 n^2}{2\pi} - \frac{\rho - \rho'}{\rho + \rho'} \frac{g\lambda^2}{4\pi^2} \right)$$

where ρ' is the density of the air in contact with the surface. For the accuracy obtained in measuring λ the first and simpler formula is sufficiently exact.

Of the terms on the right of these equations, the first is much the larger for small waves. Hence the value calculated for T will be proportional to the cube of the wave-length and to the square of the frequency. Here is the first objection to this method. The value found for T will be only one-third as accurate as the measurement of the wave-length, and one-half as accurate as the determination of the frequency. Again, since the formulæ are deduced for waves of infinitely small amplitude, we must use very moderate vibrations and these are difficult to measure.

Several, among whom we need mention only Matthiessen, Riess, and Ahrendt, have attempted to test experimentally the extreme accuracy of Lord Kelvin's formula.

When a needle is placed so that its point dips slightly into a jet of water, a series of stationary waves is formed behind the needle, and their length is equal to that of waves whose velocity is equal to the velocity of the surface of the jet at that point. This is the method employed by Ahrendt.² He found that the value of the surface tension calculated from the observed wave-length is too great but that it decreases as the needle is removed from the orifice. This proved that the fault lay in assuming that the surface of the jet moves with the velocity calculated for the ideal case. In reality, the surface has a smaller velocity, probably owing to friction with the edge of the orifice and with the air. Hence he proved nothing, so far as the formula is concerned.

Both Reiss³ and Matthiessen⁴ failed to satisfy two of the conditions

¹ Hydrodynamics, p. 446.

² Exner's Rep. der Phys., 24, 318, 1888.

³ Exner's Rep. d. Phys., 26, 102, 1890.

⁴ Pogg. Ann., 134, 107; 141, 375; Wied. Ann., 32, 626; 38, 118.

which were assumed by Lord Kelvin in obtaining his formula. One of these is that the amplitude of the waves shall be very small in comparison with the wave-length; and the other is that the surface of the liquid may be represented by an equation of the form

$$y = a \sin (mx + nt)$$

i. e., the formula is deduced for the case of a single series of very small, plane waves. The waves employed by these observers were of such an amplitude that they could be easily seen with the unaided eye; this alone might very probably introduce a discrepancy between the observed and calculated values for the wave-length. This applies to all measurements made by them. Most of their observations were made on the interference waves produced on the surface of a liquid when a vibrating fork is supported vertically above it so that two needles, one attached to either prong, may dip into the liquid. This gives two series of circular waves and so the second condition mentioned above is not fulfilled. I do not know how much this would affect the result, but until it is proved to have no affect the results must be considered as nugatory. Riess¹ says "Der Schlüssel für die definitive Lösung ist in einer minutiösen Messung der Amplituden zu suchen" and he goes on to say that the only sure method is an optical or photographic one. Matthiessen found that the formula gives results in accord with his observations except in the neighborhood of the minimum value of the velocity.

C. M. Smith² employed this method for determining the surface tension of mercury, but obtained very erratic results. Lord Rayleigh³ thinks he obtained waves due the suboctave of his fork, and these are almost sure to have too large an amplitude.

W. Ochse⁴ attempted to determine the surface tension of solution by means of ripples. He measured the interference pattern of two series of circular waves, as Riess and Matthiessen had done, his waves had a large amplitude, he assumed that the density did not

¹ Exner's Rep. d. Phys., 26, 131, 1890.

² Proc. Roy. Soc. Edinb., 17, 115.

³ Phil. Mag. (5), 30, 386 1890.

⁴ Exner's Rep. d. Phys., 26, 641, 1890.

enter into the equation, and he used rather concentrated solutions. His measurements of the wave-length are quite rough, so that the results have but little value even when corrected for the density.

From this it is seen that the formula has not been disproved, and the fact that Lord Rayleigh obtained the same value of the surface tension of water with two forks of different frequencies, and that the result obtained for water in this work agrees, within his experimental error, with Lord Rayleigh's seems to justify the application of Lord Kelvin's formula to these two cases.

All the work so far described has been with waves easily visible, and these very probably have an amplitude too large to allow the application of Lord Kelvin's formula. Lord Rayleigh was the first to use waves invisible under ordinary conditions. This method was to have the waves generated by means of a plate of glass which was attached to the lower prong of a vibrating fork, and which dipped into the liquid to be experimented upon. Then "in order to see the waves well, the light was made intermittent in a period equal to that of the waves, and Foucault's optical method, for rendering visible small departures from truth in plane or spherical reflecting surfaces, was employed." The liquid was contained in a shallow porcelain tray, and its surface was cleaned by a flexible brass hoop wider than the depth of the liquid. This was placed in the liquid so as to include the plate that generates the ripples, but otherwise in as contracted a position as possible. It was then expanded to its maximum extent. This gives a fresh surface as clean as the body of the liquid. The mean of his results for water is $T=74$ dynes per centimeter at 18° centigrade, and this is probably correct to about one per cent.

DESCRIPTION OF APPARATUS.

I shall now describe the apparatus used in this work, and which is simply a natural development of Lord Rayleigh's, although it contains many new features.

The arrangement of apparatus is represented diagrammatically in Fig. 1. S is a sixteen candle powder incandescent electric lamp; S_2 consists of two narrow strips of thin copper, one of which is fastened to each prong of the large tuning fork (F_1) (see Fig. 2), and each has

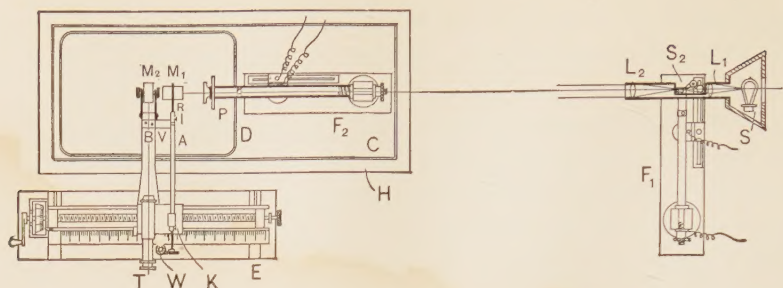


Fig. 1.

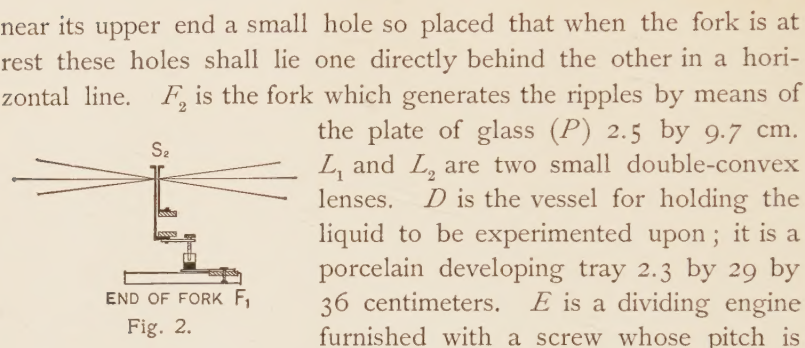


Fig. 2.

near its upper end a small hole so placed that when the fork is at rest these holes shall lie one directly behind the other in a horizontal line. F_2 is the fork which generates the ripples by means of the plate of glass (P) 2.5 by 9.7 cm. L_1 and L_2 are two small double-convex lenses. D is the vessel for holding the liquid to be experimented upon; it is a porcelain developing tray 2.3 by 29 by 36 centimeters. E is a dividing engine furnished with a screw whose pitch is 1.0328 millimeters. M_1 and M_2 are silver-on-glass mirrors. T is a telescope. To the carriage of the dividing engine is rigidly fastened a wooden arm (B) and a brass tube (A); the tube is parallel to the wooden arm and is fastened to it by means of V . To the end of B is fastened the mirror M_2 by means of brass mountings that allow it to be turned and clamped in any position desired. Through the tube A passes a brass rod (R) to which is fastened the mirror M_1 . This allows M_1 to be rotated about the axis of the tube, and it is clamped in the necessary position by means of the screws I and K . W is an iron weight hung from a rod fastened to the carriage, and is intended to counterbalance the rod, mirrors, etc.

To protect the liquid as well as possible from dust and other impurities in the air, the tray D and the fork F_2 were placed in the galvanized iron box (C) which was closed by a tightly fitting lid provided with a window of good, *plane, parallel* plate glass, through which all readings were taken.

The fork F_1 is an ordinary electrically driven tuning fork pro-

vided with a mercury platinum contact maker. F_2 is also an electrically driven tuning fork. It is tuned in unison with F_1 , and is driven by it by means of a shunt circuit.

By means of L_1 the light from S is focused on a point midway between the two holes in S_2 ; it then passes through L_2 which renders it parallel, then it is reflected by M_1 to the surface of the liquid, from this it is reflected to M_2 , and from M_2 into the telescope T . If now the forks are started and the telescope is focused for the light reflected from the crests of the waves, the entire field of the telescope, which is dimly illuminated, will be crossed by a series of parallel bright lines which correspond to the crests of the waves. These lines appear stationary, and the distance between them is approximately one-half the wave-length, since each wave is seen in two positions, once when the prongs of F_1 pass through their positions of equilibrium and are approaching one another; and again when they are separating. The crests seen in one position do not lie exactly midway between those seen in the other.

The plan of operation is to set the spider line of the telescope on one of these lines, read the position of the carriage, then move it along several centimeters, and set on another line of the same series. The difference of these two readings divided by the number of waves passed over gives the wave-length.

SOURCES OF ERROR AND ADJUSTMENTS.

The first objection that presents itself is that, as the carriage is moved, the mirrors will not remain parallel to their original positions. Owing to the length of the arms supporting the mirrors (30 cm.) and to the distance of the liquid below the mirrors (45 cm.), any slight displacement of the mirrors will produce a great error in the determination of the wave-length. These errors may be introduced either by irregularities in the ways of the engine, or by a motion of the arms with respect to the carriage. The latter is simply a matter of rigid connections and can be easily remedied, so we shall first consider the former.

To test the accuracy of the ways, the rotation of the carriage was tested about three rectangular axes—one along the screw, another horizontal and perpendicular to the screw, and the third ver-

tical. To do this, a mirror was mounted on the carriage perpendicular to the length of the screw, and a telescope (placed about ten feet from it) was focused on the image in the mirror of a vertical scale fixed to the telescope. If the carriage rotates about a horizontal axis perpendicular to the screw, the image of the scale will be displaced vertically with respect to the spider lines of the telescope. The carriage was moved several times over the entire length of the ways, but no displacement of the scale was noticed, except what might be due to changing my position with respect to the stand on which the telescope was supported.

The rotations about the other axes were tested in a similar manner and with the same result. This proved that the irregularities of the ways are at most very slight.

To test the rigidity of the arms and mirror clamps, the carriage was screwed along until the spider line in the telescope on the carriage coincided with a well defined crest. It was then slipped back, leaving the nut in place on the screw, and again moved up by hand to the nut. The line again coincided with the crest. This proved that moving the carriage by hand produced no effect on the relative positions of the carriage and its appurtenances. The carriage was then again slid from the nut, and, while held with one hand it was struck several sharp, horizontal taps with a block of soft wood. It was then moved back against the nut. If the telescope and mirrors are clamped tightly the line again coincides with the crest. This proves that slight jars of the screw will introduce no error into the results if the telescope and mirrors are well clamped.

Having settled this point, the other adjustments, which will now be described, were made; and then the ways were again tested by a method which will be described further on, and which is much more delicate than the one first used.

Leaving aside the accuracy of the screw and the motion of the carriage, there are six fundamental adjustments to be made.

1. The carbon filament and the axes of the lenses L_1 and L_2 must lie in a straight line.
2. The beam of light must be composed of parallel light and
3. It must be horizontal before reflection by M_1 ;
4. The ways of the engine must be horizontal and at such a height that the beam of parallel light may strike the mirror M_1 , and

5. They must be parallel to the beam of light ;

6. The fork F_2 must be parallel to the ways of the engine. This is easily adjusted by means of a plumb line hung from the rod R .

1. The lenses L_1 and L_2 are placed in a tin tube against diaphragms perpendicular to the axis of the tube. This makes their axes practically coincide. The lamp S is then adjusted so that the light (from the filament that is to be used) after passing through L_1 covers the centre of L_2 . Then the filament and the axes of L_1 and L_2 are in a straight line.

2. The lense L_1 is moved until the light is focused on S_2 and then L_2 is moved until on reflecting the beam of light back along its original path, it appears to converge to the hole in S_2 , through which it originally came. The position of L_2 is then adjusted until the light is as nearly parallel as one can detect with a small telescope focused for infinity.

3. The entire system L_2 , L_1 and S , is then inclined by leveling screws until the beam of light is as nearly horizontal as can be detected by means of a water level two meters long.

4. The engine is placed on a slab of slate mounted on leveling screws and at the desired height. The horizontality of the ways is tested by means of a delicate spirit level.

5. If two strips of paper are pasted on M_1 so that their edges touch opposite sides of the part of M_1 that is covered by the beam of parallel light ; and if the engine is moved until the light remains on this spot while the carriage is moved over the entire length of the ways (about 50 cm.) we may be sure that the ways are quite approximately parallel to the beam of parallel light.

If water is now placed in the tray, if the mirrors and the telescope are turned so that the light is thrown down the tube of the telescope, and if cross-threads are stretched across L_2 , a dark cross will be seen in the field of the telescope when it is focused for a point about one meter below the surface of the water (which is the focal length used throughout this work). The cross-threads in the telescope are made to coincide with this cross, and the carriage is moved along the ways.

If the ways are accurate, and if the other adjustments have been well made, these crosses will coincide throughout the length of the

screw. But, owing to slight irregularities in the ways, it is found that the crosses are relatively very slightly shifted, though from scale reading 15 to scale reading 29 they remained coincident, except from 22.6 to 24.3 where one bearing of the carriage rests upon a slight dent in one of the ways. Hence, all settings were taken between 16.5 and 22, and between 25 and 27. In these regions I could detect not the slightest shift; so I think the readings are entirely free from any error due to inaccuracies in the ways. Any error in the other adjustments also causes a shift in the positions of the crosses, but this is uniform throughout the length of the ways, and so can easily be distinguished from the nonuniform displacement due to faults in the ways.

EXTRANEOUS DISTURBANCES.

Having disposed of these difficulties we come to another that gave great trouble. This is the disturbance of the liquid by extraneous vibrations. After trying many plans I finally placed the box containing the tray of water and the fork F_2 upon an iron slab (H) weighing almost 150 pounds, and supported by long steel springs hung from a joist whose ends rested in the walls of the building but which was free from the floor above. It was hung so that when weighted for work it was about three or four centimeters above the top of a brick pier, and the intermediate space between it and the pier was loosely filled with cotton batting. If the cotton is packed neither too tightly nor too loosely, this arrangement cuts out most extraneous disturbances. The dividing engine was supported on this pier. The fork which generated the ripples, and the vessel of water were each supported on pieces of rubber tubing so that the water might not be disturbed by any slight vibration of the stand of the fork.

(*To be concluded.*)

THE SURFACE TENSION OF WATER AND OF CERTAIN DILUTE AQUEOUS SOLUTIONS, DETERMINED BY THE METHOD OF RIPPLES. II.

(*Concluded.*)

BY N. ERNEST DORSEY.

INFLUENCE OF GLASS PLATE.

ANOTHER point of prime importance is to have the glass plate, which generates the waves, well wetted by the liquid. If it is not, the crests will be so irregular and so distorted that no correct setting can be made. A microscope slide was first used but it was very difficult to get its surface in such a condition that water would wet it readily, and one lot of slides I was entirely unable to use; I tried to clean them with caustic potash, sulphuric acid, nitric acid, chromic acid; I even boiled them in chromic acid, and still water would not readily wet them, and never under any condition did I succeed in wetting them uniformly. I finally used a piece of thin German plate mirror from which the silvering was removed. This was easily cleaned and there was no trouble in keeping it in such a condition that water and salt solutions would wet it readily and uniformly.

When I began this work I always took one reading within two centimeters of the fork, in order that I might run the fork with as small an amplitude as possible, so as to avoid reflected waves. The other reading was taken some five or ten waves further from the fork.

The results obtained by this method were very erratic. The wave-lengths found on any one day would agree fairly well among themselves, but those obtained on different days seldom agreed at all. Later on it was found that the apparent wave-length depended upon how many waves were included between the settings.

After trying nearly every plan that could be devised to find the

trouble it was at last decided to measure each individual wave and see if these separate determinations would throw any light on the difficulty. In this series of measurements I went as close to the fork as I could measure, and found (although these separate determinations were very rough) that the apparent wave-length *increased* as the fork was approached. As a last resort I attributed this effect to the rise of the liquid against the plate which generates the ripples, although I did not think that this could effect waves two centimeters distant. To test this experimentally the plate that was well wetted was replaced by one coated with paraffin.

It was now found that the waves apparently *decreased* as the fork was approached. This proved that, contrary to expectations, the effect of the meniscus makes itself felt two or three centimeters from the fork.



Fig. 4.

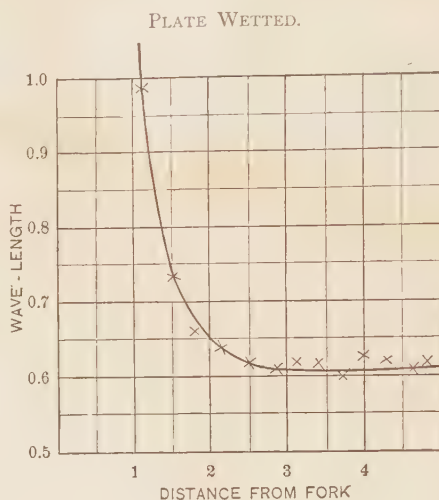


Fig. 3.

Two typical curves showing this effect are given in figures 3 and 4.

The magnitude of the error introduced in this way depends upon the amplitude of the waves, and this is probably the reason why the results obtained on different days were not comparable; for I frequently changed the amplitude of my fork so as to alter the

distinctness of the field in the telescope. Many weeks were spent in locating this error; and after finding it no reading was taken nearer

the fork than four centimeters. Under these conditions the measured wave-length does not depend upon the number of waves measured, nor upon the distance of the waves from the fork, nor upon the amplitude of the fork (so long as it is small); all these points were tested experimentally. I was very seldom troubled by reflected waves.

The mirrors M_1 and M_2 must be good plane metal mirrors. Owing to the double reflections, ordinary glass front mirrors can not be used, since in my arrangement the images overlap and distort one another. The silver surface obtained by depositing silver by Brashear's process¹ on good thin plate German mirror glass was used in this experiment.

PERIODS OF FORKS.

The fork F_2 is a large one with a mirror and a counter-weight screwed into the ends of its prongs, and belongs to a set of König forks used to show Lissajou's figures. The mirror was replaced by a second counter-weight, and the plate of glass which generated the ripples was fastened by screwing down the weight until the plate was clamped tightly between it and the end of the prong of the fork. This allowed the plate to be removed and cleaned without danger of wetting the fork. Sliding on the prongs were light brass weights that could be clamped wherever desired.

F_1 was also provided with sliding weights, and after putting on the strips of copper (S_2) I tuned it (by means of a vibration microscope) to unison with F_2 while the weights on F_2 were near the centre of its prongs, and while the plate of glass was dipping into water.

By means of the smoked glass and pendulum method the frequency of the vibration microscope, which was an octave above F_1 , was determined. It made 125.8 complete vibrations per second. Then as a check the vibration microscope was again compared with F_1 , and it was found that the ratio of their frequencies was still two to one.

The vibration microscope rather than F_1 was compared with the pendulum because it was more readily handled than the larger fork. This method, however, cannot be depended upon except to give the

¹ Astrophysical Journal, I, 252, 1895.

whole number of vibrations per second. To determine the exact frequency Michelson's method¹ was employed, but the results were carried to but two decimal places, as the frequency of a fork driven by a mercury contact does not seem to be more constant than this approximation. Now, in order to use this method, the clock must give exactly equal intervals of time ; Professor Michelson says that the intervals must differ by less than 0.002 second in rating a fork of 128 double vibrations per second. The clock at my disposal had a mercury contact, and I found that working alone I could not adjust this so accurately in the center of the arc of the pendulum as is required for consistent results. In any case, as Professor Michelson states, a mercury contact is not very good unless it is quite narrow in the direction of the swing of the pendulum.

After trying many contacts and after working on the subject for some time, I finally devised one that is very simple and has so far given perfect satisfaction. A contact is desired that can be easily adjusted so as to give absolutely equal intervals of time ; so it seemed the best method would be to use the complete period of the pendulum instead of the half period, as is ordinarily adopted. This would obviate the difficulty of centering the apparatus.

The construction of the contact is as follows : A steel watch spring about 8 cm. long is soldered to a brass collar which is fastened by means of a screw to one end of a brass plate 4 cm. wide and 10 cm. long. The collar can be rotated about the axis of the screw, and clamped tightly at any angle desired. Perpendicular to the flat surface of the spring and about 5 cm. from the collar is soldered a platinum point which, when the spring is slightly depressed, dips into mercury in a cup attached to the brass plate but insulated from it. At the same place and perpendicular both to the platinum point and to the length of the spring is soldered the point of a fine steel sewing needle. This needle point must be quite fine and well polished. At the further end of the spring is fastened a mica vane which dips into oil contained in another cup fastened to the brass plate, and is intended to damp the vibrations of the spring. The brass plate to which these parts are attached is fastened to the back of the clock near the top of the pendulum and in such a posi-

¹ Phil. Mag. (5), 15, 84-87, 1883.

tion that the needle point comes near the centre of the arc of the pendulum.

To the pendulum rod is fastened a light brass collar on the back of which is soldered a short piece of steel watch spring which projects horizontally from the rod, and whose plane is inclined to the rod at an angle of about 50° or more. The lengths of the needle point and of this short piece of spring are such that when they are in place, and the pendulum is at rest they overlap by an amount just sufficient to ensure the depressing of the point at each complete vibration of the pendulum. Both sides of the short spring are carefully polished, and the collar is so adjusted that the needle point comes just below the upper edge of the spring. The electric circuit is completed through the long spring and the mercury cup. Then when the pendulum swings in one direction the platinum point is depressed into the mercury and closes the circuit, and immediately rises and breaks it as the pendulum swings on; on the return swing the platinum point is slightly raised. If the damping vane works properly the vibrations of the spring will be practically dead beat, and we shall have contact made once only during each complete vibration of the pendulum.

Dr. J. F. Mohler kindly compared the clock I used with the astronomical one and found that each single swing of the pendulum corresponds to 1.000397 seconds; the mean solar day being the unit of time. Hence we are justified in taking the complete period of the pendulum as two seconds.

As any change in the positions of the blades S_2 affect the period of the fork, its frequency was often determined so as to avoid errors due to careless handling.

AMPLITUDE OF WAVES.

We have seen that Lord Kelvin's equation applies to waves of infinitely small amplitude, so it is well to consider the amplitude of the waves used in this work. I have no way to measure its value directly, but a general idea of its smallness may be obtained by considering the fact that throughout the work the telescope was focused for a point one meter below the surface of the liquid. Since the beam of incident light is parallel, this means that in the neighbor-

hood of a crest the radius of curvature is about two meters. This, together with the fact that these waves are only 0.48 cm. long, shows that their amplitudes must be extremely small. We can also see that the amplitudes are very small from the effect of the meniscus upon the apparent length of the waves at such a great distance as two centimeters from the plate (page 27).

EFFECT OF VISCOSITY.

Before going further it is well to consider another point. How does the viscosity of the liquid affect the apparent wave-lengths? Professor Tait¹ has shown that viscosity does not affect the true wave-length, but simply introduces a damping factor of the form ε^{ax} , where a depends upon the wave-length and the viscosity of the liquid. Hence the apparent wave-length is the distance between the corresponding consecutive points where the curve $y = A\varepsilon^{-ax} \sin mx$ has a constant slope c . Hence it is necessary to find the roots of the equation.

$$\frac{dy}{dx} = -Aa\varepsilon^{-ax} \sin mx + Am\varepsilon^{-ax} \cos mx = c$$

or

$$B \cos (mx + \partial) = \frac{c}{A} \varepsilon^{+ax} \text{ where } B = \sqrt{a^2 + m^2}, \tan \partial = \frac{a}{m}.$$

Since a is very small for water and dilute solutions, B is approximately equal to m . The maximum value of c is at the point $x=0$, where $c=Am$. Hence the roots of the equation are the abscissæ of the points of intersection of the curves

$$z = \cos (mx + \partial) \text{ and } z = E\varepsilon^{ax} = E(1 + ax)$$

approximately; $E \neq 1$. By setting near a crest E can be made very small and hence the slope of the line $z = E\varepsilon^{ax}$ will also be small, practically zero, and the apparent wave-length must be very nearly $\frac{2\pi}{m}$, which is the true wave-length. If we could make $c=0$; the apparent and real wave-lengths would be exactly equal.

To test experimentally the error that might be introduced if c were

¹ Proc. Roy. Soc. Edinb., 17, 110-115, 1890.

not zero, the telescope was turned so as to look on one side of the crests at points having as great a slope as could be observed, and the apparent wave-length was measured. The telescope was then turned so as to look at corresponding points on the other side of the crests and the wave-length was again determined. Each time I measured over a distance equal to 20 waves, the interval usually employed in the rest of the work. The maximum difference observed amounted to one-fifth of one per cent.

The apparent field swept over by the spider line in turning the telescope from one of these positions to the other is over two centimeters; and I can easily adjust the line to the centre of this field to within one millimeter, *i. e.*, one-twentieth of the total angle through which I turned the telescope. If the error was proportional to the angle, this would correspond to 0.01 per cent; but the error varies almost as the cosine of the angle. Hence the error introduced is negligible.

EFFECT OF PARTICLES.

In this same article Professor Tait shows that the effect of a "uniform film of oxide or dust, in *separate* particles which adhere to and move with the surface" is to increase the wave-length if there is no viscosity. If terms involving the first power of the viscosity must be taken into account, the surface layer will not affect the wave-length, but will aid viscosity in causing the waves to subside as they advance.

WATER AND SALTS.

The water used in these experiments was especially distilled by Dr. W. T. Mather, and was the kind he used for his electrolytic work. He distilled it from chromic acid, and from potassium permanganate, and condensed it in a block tin condenser. It was collected in a bottle used for no other purpose, and which was kept always covered or stoppered. It was transferred from this to a larger bottle that had a hole bored near its bottom so that the water could be drawn off through a piece of black rubber tubing and a glass nozzle. This tube and nozzle always remained filled with water, which protected their inner surfaces from impurities in the air. The glass nozzle was removed and cleaned before drawing the water. In

this way it was hoped to get water as pure as possible. I might mention here that the water and solutions used in this work were not free from air; but Röntgen and Schnicker¹ have shown that the effect of dissolved air is entirely negligible at ordinary pressures.

I used Eimer and Amend's chemically pure salts.

The temperatures of the water and solutions were determined by means of a Bender and Hobein thermometer of Normalglas graduated to tenths of a degree centigrade.

The densities of the solutions of sodium chloride, of sodium carbonate, and of zinc sulphate were calculated from the values given by Kohlrausch and Hallwachs²; those for potassium chloride from the results obtained by Bender³; and those for potassium carbonate from Gerlach's values as given in Landolt and Börnstein's "Physikalisch-Chemische Tabellen." The densities for water were taken from Marek's values.⁴

METHOD OF OBSERVATION.

Before each series of readings the tray, the glass plate, the brass hoop for cleaning the surface of the liquid, the thermometer, and the stirring rod were washed, first with tap water, then with an alcoholic solution of caustic potash, then with running tap water, then with chromic acid, and finally they were well rinsed in running tap water. Then everything was placed in position in the iron box, water was run into the tray until the lower edge of the glass plate dipped just under the surface. I then expanded the hoop, put the lid on the box, and brought the iron slab to rest as soon as possible. Then the forks were set in vibration, the spider line of the telescope was brought into coincidence with a crest near the middle of the pan, and the amplitude of the vibrations was increased until the crest was almost out of focus. As stated before, the waves appear stationary. Then the shunt circuit by which F_2 was run was broken and the fork was allowed to come to rest at its free period. The fork F_1 being still vibrating, the crests will have an apparent motion unless the free period of F_2 coincides with the period of F_1 . If the two did not coincide the weights on F_2 were moved until they did. By care

¹ Wied. Ann., 17, 207, 1882.

³ Wied. Ann., 22, 179, 1884.

² Wied. Ann., 53, 14, 1894.

⁴ Wied. Ann., 44, 171, 1891.

the depth of the water can be adjusted so that this correction is seldom necessary; but unless the two forks are in unison the crests are almost sure to oscillate, on account of the imperfection of the mercury contact. The plate which generates the waves should never leave the liquid, but it should dip below the surface as little as possible. If it dips deeply into the liquid the waves always appear distorted.

Having brought the forks to unison the spider line is brought successively into coincidence with three consecutive crests near scale division 17. Then the carriage is screwed along and readings are taken on the fortieth, forty-first and forty-second crest beyond the one on which the first setting was made. The thermometer is then read, the hoop is lifted from the water, is contracted, replaced into the water and expanded, and another series of six readings is taken. Then a known weight of salt is added, and the solution is stirred until the salt is dissolved. Then readings are taken as for water; then more salt is added, and so on until readings have been taken on water and on solutions of (as a rule) four different concentrations. Then the volume of the solution is measured. I measure the volume last so that the purity of the water may not be affected by any trace of grease that might be on the measuring vessel.

Since each crest is seen in two positions, measuring over forty crests gives the length of twenty waves. Such a series of readings as I have just described occupies about two hours; and to make sure that the surface in this length of time does not become contaminated so as to affect my results, a check series was taken on water. The first readings gave $T_{180.9}=73.10$ or $T_{180}=73.24$; the last, about two and one-half hours later, gave $T_{180.3}=72.91$, or $T_{180}=73.18$. Hence the results obtained from such a series of readings that extend over about two hours should be not appreciably affected by the contamination of the surface by the air.

By this plan of work we obtain for each concentration two sets of three independent determinations of the wave-length. If the average of these two sets agree fairly well, the surface tension is calculated from their mean. If they do not agree well another series is taken and the surface tension is calculated from the weighted mean of the three series.

TEMPERATURE REDUCTION.

To reduce the results to the standard temperature, eighteen degrees centigrade, I used the formula $T_t = T_0 (1 - \alpha t)$, and took $\alpha = 0.0020$ which is the average of the following values :

Brunner	0.0019	Pogg. Ann., 70, 481.
Braun	0.0020	Winklemann, Handb. d. Phys., I., p. 467.
Frankenheim	0.0018	Pogg. Ann., 72, 177, 222, 1847.
Wolf	0.0018	Ann. de chim. et de phys. (3), 49, 269, 1857.
Volkmann	0.0018	Wied. Ann., 17, 353, 1882.
Timberg	0.0022	Wied. Ann., 30, 545, 1887.
Jäger	0.0023	Acad. de Wiss. in Wien., 100, 245, 1891.
Cantor	0.0021	Wied. Ann., 47, 399, 1892.
Humphreys and Mohler	0.0020	Phys. Review, 2, 387, 1895.
Sentis	0.0020	J. de Phys. (3), 6, 183, 1897.
	0.0020	

In this formula t is the temperature in degrees centigrade ; T_t is the surface tension at $t^\circ\text{C}.$; and T_0 is the surface tension at $0^\circ\text{C}.$

Since the salt solutions used were very dilute I used the same temperature coefficient (0.0020) for them ; Sentis says that in any case the temperature coefficient for aqueous salt solutions differs from that for water by an amount less than his experimental error, which is about the same as mine.

RESULTS.

The results obtained are given in the tables and are represented graphically in Fig. 5.

In the tables the concentration of the solution is given in gram molecules per liter, and is placed in the column marked $\frac{\text{gm. mol.}}{\text{liter}}$; t denotes the temperature in degrees centigrade ; n is the frequency of the fork ; ρ is the density ; T_t is the surface tension at $t^\circ\text{C}.$, and T_{18} is the surface tension at $18^\circ\text{C}.$; both T_t and T_{18} are expressed in dynes per centimeter ; λ_1 is the observed wave-length in terms of scale divisions of the engine, one division = 1.0328 cm.

TABLE I.

NaCl						
Gm. mol. liter.	t	n	λ_1	$\frac{T_t}{\rho}$	T_t	T_{18}
.0	16.0	63.07	0.4858	73.72	73.64	73.34
0.067	17.2	"	0.4852	73.44	73.56	73.44
0.14	17.8	"	0.4849	73.29	73.58	73.55
0.22	18.2	"	0.4843	73.01	73.57	73.60
0.29	18.6	"	0.4843	73.01	73.78	73.87

NaCl.						
.0	16.3	63.07	0.4858	73.72	73.64	73.38
0.12	16.7	"	0.4852	73.44	73.70	73.50
0.29	17.4	"	0.4849	73.29	74.08	73.99
0.46	17.7	"	0.4840	72.88	74.16	74.12
0.63	18.5	"	0.4837	72.73	74.37	74.45

NaCl.						
.0	13.1	63.07	0.4865	74.03	73.99	73.25
0.17	13.5	"	0.4859	73.76	74.23	73.55
0.33	14.1	"	0.4855	73.57	74.52	73.92
0.51	15.0	"	0.4854	73.52	75.00	74.54
0.68	19.0	"	0.4841	72.92	74.83	74.99

NaCl.						
.0	16.4	62.96	0.4863	73.67	73.59	73.35
0.088	17.0	"	0.4860	73.54	73.72	73.57
0.17	17.3	"	0.4855	73.30	73.73	73.62
0.25	17.4	"	0.4849	73.01	73.68	73.59

NaCl.						
.0	18.6	62.96	0.4854	73.25	73.14	73.23
0.37	19.3	"	0.4839	72.56	73.55	73.75
0.72	19.8	"	0.4825	71.91	73.91	74.17
1.11	20.1	"	0.4815	71.45	74.53	74.86
1.46	20.0	"	0.4805	70.99	75.02	75.33

TABLE I.—*Continued.*

NaCl.						
Gm. mol. liter.	t	n	λ_1	$\frac{T_t}{p}$	T_t	T_{18}
.0	19.3	62.96	0.4842	72.69	72.57	72.77
0.397	20.3	"	0.4837	72.47	73.53	73.88
0.468	20.9	"	0.4837	72.47	73.72	74.17
0.549	21.3	"	0.4833	72.28	73.76	74.27
0.62	21.4	"	0.4824	71.86	73.54	74.06
0.703	21.3	"	0.4817	71.55	73.46	73.97
0.768	21.2	"	0.4821	71.73	73.83	74.32

NaCl.						
.0	15.9	62.96	0.4860	73.54	73.47	73.15
0.34	16.2	"	0.4852	73.16	74.11	73.84
0.40	16.5	"	0.4850	73.06	74.19	73.96
0.46	16.8	"	0.4845	72.76	74.06	73.88
0.52	16.9	"	0.4847	72.92	74.40	74.23
0.58	17.1	"	0.4841	72.65	74.30	74.16
0.64	17.2	"	0.4840	72.56	74.38	74.26
0.76	17.3	"	0.4840	72.56	74.72	74.61
0.88	17.4	"	0.4831	72.19	74.69	74.60

KCl.						
.0	18.6	62.87	0.4854	73.02	72.91	73.00
0.09	18.6	"	0.4861	73.35	73.49	73.58
0.19	18.4	"	0.4858	73.21	73.76	73.82
0.27	18.3	"	0.4852	72.93	73.75	73.80
0.35	18.2	"	0.4853	72.98	74.05	74.08
0.58	18.1	"	0.4855	73.07	74.52	74.54

KCl.						
.0	18.7	62.78	0.4855	72.84	72.73	72.84
0.338	19.3	"	0.4851	72.66	73.68	73.88
0.557	19.9	"	0.4849	72.57	73.96	74.25
0.771	20.2	"	0.4839	72.11	74.55	74.89
0.986	20.3	"	0.4827	71.56	74.62	74.98
1.204	20.3	"	0.4823	71.37	75.11	75.48

TABLE I.—*Continued.*

KCl.						
Gm. mol. liter.	t	n	λ_s	$\frac{T_t}{\rho}$	T_t	T_{18}
.0	18.0	62.87	0.4863	73.43	73.33	73.33
0.19	17.3	"	0.4851	72.88	73.44	73.33
0.37	16.8	"	0.4847	72.69	73.86	73.68
0.55	16.4	"	0.4847	72.69	74.46	74.21
0.73	16.0	"	0.4844	72.55	75.00	74.69
0.92	15.8	"	0.4836	72.19	74.96	74.62

KCl.						
.0	21.1	62.78	0.4860	73.08	72.81	73.28
0.221	20.6	"	0.4848	72.52	73.14	73.54
0.446	20.3	"	0.4843	72.29	73.64	73.99

$\frac{1}{2}(\text{K}_2\text{CO}_3 + 2 \text{ aq})$						
.0	18.3	62.86	0.4862	73.38	73.28	73.33
0.22	19.2	"	0.4850	72.82	73.85	74.04
0.44	19.9	"	0.4833	72.04	73.97	74.27
0.66	20.4	"	0.4813	71.13	73.90	74.27
0.88	20.8	"	0.4802	70.61	74.41	74.84

$\frac{1}{2}(\text{K}_2\text{CO}_3 + 2 \text{ aq})$						
.0	13.7	62.86	0.4864	73.46	73.41	72.76
0.096	13.7	"	0.4860	73.28	73.81	73.16
0.294	13.6	"	0.4851	72.86	74.29	73.62
0.512	13.5	"	0.4836	72.17	74.43	73.74
0.713	13.5	"	0.4826	71.70	74.95	74.26
0.915	13.5	"	0.4812	71.07	75.14	74.45

$\frac{1}{2}(\text{Na}_2\text{CO}_3 + 10 \text{ aq})$.						
.0	18.5	62.85	0.4857	73.11	73.00	73.08
0.061	18.5	"	0.4855	73.02	73.20	73.28
0.187	18.1	"	0.4853	72.92	73.61	73.63
0.310	17.6	"	0.4849	72.74	73.95	73.89
0.432	17.4	"	0.4840	72.33	74.04	73.95

TABLE I.—*Continued.*

$\frac{1}{2}(\text{Na}_2\text{CO}_3 + 10 \text{ aq.})$						
Gm. mol. liter.	t	n	λ_1	$\frac{T_i}{\rho}$	T_t	T_{18}
.0	17.9	62.86	0.4857	73.14	73.04	73.03
0.115	17.6	"	0.4855	73.05	73.42	73.36
0.228	17.1	"	0.4848	72.73	73.54	73.40
0.344	16.6	"	0.4848	72.73	74.02	73.81
0.458	16.3	"	0.4838	72.27	73.99	73.73
0.574	15.9	"	0.4837	72.22	74.40	74.08

$\frac{1}{2}(\text{ZnSO}_4 + 7 \text{ aq.})$						
.0	18.1	62.78	0.4867	73.40	73.30	73.31
0.129	18.7	"	0.4850	72.65	73.32	73.43
0.257	18.7	"	0.4840	72.16	73.58	73.69
0.39	18.7	"	0.4822	71.47	73.64	73.75

$\frac{1}{2}(\text{ZnSO}_4 + 7 \text{ aq.})$						
.0	17.7	62.78	0.4864	73.26	73.16	73.12
0.283	18.2	"	0.4832	71.79	73.36	73.39
0.567	18.4	"	0.4804	70.51	73.65	73.71

$\frac{1}{2}(\text{ZnSO}_4 + 7 \text{ aq.})$						
.0	18.6	62.78	0.4867	73.40	73.12	73.21
0.115	19.6	"	0.4853	72.76	73.33	73.58
0.173	19.7	"	0.4851	72.66	73.48	73.74
0.216	19.7	"	0.4845	72.38	73.54	73.80
0.263	19.7	"	0.4832	71.79	73.22	73.48

$\frac{1}{2}(\text{ZnSO}_4 + 7 \text{ aq.})$						
.0	18.4	62.78	0.4866	73.35	73.24	73.31
0.0435	19.5	"	0.4857	72.94	73.07	73.30
0.0887	20.2	"	0.4847	72.47	72.88	73.38
0.133	20.7	"	0.4850	72.61	73.28	73.69
0.35	20.5	"	0.4832	71.79	73.71	74.09

TABLE I.—*Concluded.*

$\frac{1}{2}(\text{ZnSO}_4 + 7 \text{ aq.})$						
Gm. mol. liter.	z	n	λ_1	$\frac{T_t}{\rho}$	T_t	T_{18}
.0	18.3	62.78	0.4868	73.45	73.34	73.39
0.0199	18.4	"	0.4860	73.08	73.11	73.17
0.066	18.8	"	0.4856	72.89	73.18	73.30
0.108	18.9	"	0.4853	72.76	73.30	73.44
0.152	18.7	"	0.4850	72.61	73.42	73.52
0.286	18.7	"	0.4841	72.21	73.80	73.90
0.330	18.5	"	0.4830	71.71	73.54	73.62
0.372	18.4	"	0.4829	71.65	73.75	73.79
0.414	18.3	"	0.4827	71.55	73.87	73.91

$\frac{1}{2}(\text{ZnSO}_4)$						
.0	14.8	62.85	0.4870	73.74	73.68	73.20
0.18	15.2	"	0.4848	72.70	73.72	73.30
0.37	15.5	"	0.4839	72.31	74.43	74.05
0.555	15.9	"	0.4822	71.53	74.67	74.35
0.736	16.2	"	0.4804	70.71	74.82	74.54
0.919	16.4	"	0.4789	70.03	75.06	74.81

In the first series for potassium chloride the two forks were not in unison when the surface tension of water was determined, but were afterwards adjusted. This accounts for the low value found for water. In the case of the carbonates, for which but two series of determinations were made, the two sets of points are denoted on the plate by crosses and by crosses in circles respectively. It will be noticed that the two series for potassium carbonate do not coincide but lie parallel to one another. If there were any impurity in the body of the water that decreased its surface tension, it could not be removed by the flexible hoop, and probably would lower the whole curve as we observe in this case. Those points for zinc sulphate which are represented by crosses in circles were obtained from a series of readings on solutions of the anhydrous sulphate. This contained quite a little of the sulphide, which floated around in the solution but which apparently produced no effect on the wave-lengths of the ripples. The values obtained by Sentis are represented by circles.

It is evident that these results can be best represented by straight lines. If we write

$$T_s = T_w + Kc$$

where T_s is the surface tension of the solution containing c gram-equivalents per liter, and T_w is the surface-tension of water at the same temperature, and K is a constant, we find K from the plotted results. The values found for K by various observers are given in the following table: those assigned to Sentis were calculated from his observations on solutions of 0.56 and 1.13 normal concentrations.

TABLE II.

H ₂ O						
t	n	λ_1	$\frac{T_t}{\rho}$	T_t	T_{18}	T_0
16.0	63.07	0.4858	73.72	73.64	73.34	
16.3	63.07	0.4858	73.72	73.64	73.38	
13.1	63.07	0.4865	74.03	73.99	73.25	
16.4	62.96	0.4863	73.64	73.59	73.35	
18.6	62.96	0.4854	73.25	73.14	73.23	
19.3	62.96	0.4842	72.69	72.57	72.77	
15.9	62.96	0.4860	73.54	73.47	73.15	
18.6	62.87	0.4854	73.02	72.91	73.00	
18.7	62.78	0.4855	72.84	72.73	72.84	
21.1	62.78	0.4860	73.08	72.81	73.28	
18.0	62.87	0.4863	73.43	73.33	73.33	
18.3	62.86	0.4862	73.38	73.28	73.33	
13.7	62.86	0.4864	73.46	73.41	72.76	
17.9	62.86	0.4857	73.14	73.04	73.03	
18.5	62.85	0.4857	73.11	73.00	73.08	
18.1	62.78	0.4867	73.40	73.30	73.31	
17.7	62.78	0.4864	73.26	73.16	73.12	
18.6	62.78	0.4867	73.40	73.12	73.21	
18.4	62.78	0.4866	73.35	73.24	73.31	
18.3	62.78	0.4868	73.45	73.34	73.39	
14.8	62.85	0.4870	73.74	73.68	73.20	
17.44				73.25	73.17	
Omitting $T_{18} = 72.77; 72.84; 72.76$ we find the following values:						
17.48				73.32	73.24	75.98

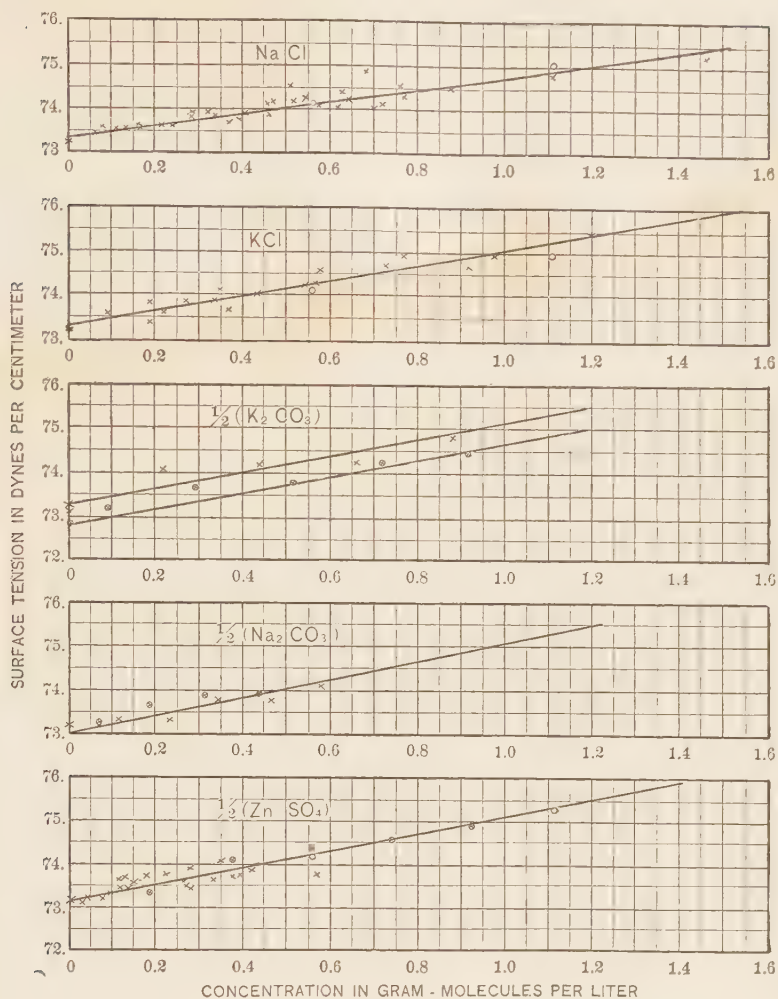


FIG. 5.

	Volkmann	Quincke	Sentis	Rother	Dorsey
NaCl; K=	1.59	1.57	1.57	1.38	1.53
KCl; K=	1.41	1.57	1.41	1.47	1.71
$\frac{1}{2}(Na_2CO_3)$; K= 0.987		1.57	—	—	2.00
$\frac{1}{2}(K_2CO_3)$; K= 1.78		1.57	—	—	1.77
$\frac{1}{2}(ZnSO_4)$; K= —		—	1.78	—	1.86

All of Volkmann's curves appear to become steeper as they approach zero concentration, and his curves for K_2CO_3 and Na_2CO_3

cross near the origin so that the curve for Na_2CO_3 for dilute solutions become steeper than the one for K_2CO_3 .

The comparison of the results of this work with those obtained by other observers must not be pushed too far, because they have worked exclusively on solutions of greater concentration than half normal, while most of my observations are on solutions less concentrated than that.

The average of all observations taken on water gives $T_{17^{\circ}.44}=73.25$, or $T_{18^{\circ}}=73.17$ which is rather low. If we omit the values $T_{18^{\circ}}=72.77$, 72.84 and 72.76 , which are certainly too low, we find the averages given in the last line of the table, viz., $T_{17^{\circ}.45}=73.32$ which gives $T_{18^{\circ}}=73.24$ and $T_0=75.98$. This is lower than the values found by Quincke, but agrees very well with the results obtained by Volkmann, Hall, Sentis, Rayleigh and others.

In conclusion I wish to thank Professor Rowland and Dr. Ames for their suggestions and encouragement throughout the entire course of the work.

JOHNS HOPKINS UNIVERSITY, May, 1897.

BIOGRAPHICAL SKETCH.

The author was born at Annapolis Junction, Maryland, on March 15, 1873. He attended the public school in the country until twelve years of age, when he entered the Friend's Elementary and High School of Baltimore, where he continued his studies until he entered the Johns Hopkins University in October, 1890. Since then he has maintained a continuous connection with the latter institution. After pursuing the undergraduate courses known as Group II., he received the degree of Bachelor of Arts in June, 1893, and then undertook graduate work in Physics, in Mathematics, and in Chemistry. He was a University Scholar in 1893-94; a Student-Assistant in Physics from October, 1893, to June, 1896, and a Fellow during the present year.

NOAH ERNEST DORSEY.

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